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Johnson, Donald L.; Wilson, Brent M.; Carr, James D.; Russell, Matthew A.; Murphy, Larry E.; and Conlin, David L., "Corrosion of Steel Shipwrecks in the Marine Environment: USS *Arizona*—Part 2" (2010). *Faculty Publications -- Chemistry Department*. 191.  
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# Corrosion of Steel Shipwrecks in the Marine Environment: USS *Arizona*—Part 2

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**This article is a continuation of Part 1 (October 2006 MP) on the USS *Arizona* hull. It discusses additional methods being investigated for use in determining corrosion rates with a minimal impact on the existing structure. Marine biofouling (concretion) has accumulated on the hull. Concretion samples have been studied using x-ray diffraction, environmental electron microscopy, and corrosion potential ( $E_{\text{corr}}$ ) to characterize the relationship between concretion and the steel substrate. The data presented in this study confirm the viability of concretion analysis as a minimum-impact procedure to estimate the corrosion rate of mild steel in seawater.**

monitoring, oil analysis, microbiology, geology, and oceanography to characterize and quantify the deterioration of the ship's hull and develop a long-term monitoring program. The data collected will provide critical input to variables used in conjunction with a finite element model (FEM), which constitutes the primary research product. The FEM provides a means to combine in situ measurements with corrosion rates to evaluate timing and the long-range consequences of management actions directed at preserving the ship's hull.

USS *Arizona* is an immensely significant national shrine, National Historic Landmark, and war grave for more than 1,100 sailors lost during the Japanese attack on Pearl Harbor on December 7, 1941. Part 1 of this article (October 2006 MP) presented the testing and results of corrosion rate measurements on coupons taken of the hull. Part 2 discusses data in support of concretion analysis as a minimum-impact method that may be used to estimate corrosion rates of submerged steel vessels.<sup>1</sup>

## Experimental Procedures

Iron accumulation in naturally forming concretion was first reported by North<sup>2</sup> and subsequently discussed by Macleod<sup>3</sup> as related to cast and wrought iron shipwrecks. North has also suggested that iron accumulation can occur in the concretion on steel, as observed in the 1980s.<sup>4</sup> The major difference between cast iron and steel corrosion is that a remnant graphitic layer is often left behind to mark the original surface of cast iron. Such a remnant does not exist on corroded steel surfaces.

## CONCRETION/METAL/OXIDE INTERACTIONS

A Siemens x-ray diffractometer<sup>†</sup> (XRD) was used to scan the cross section of a USS *Arizona* concretion sample at 1-mm (0.04-in.) intervals (Figure 1).<sup>5</sup> The phases present in the XRD patterns were determined with search-match software. Excellent fits to the observed patterns were

**T**his research was conducted as part of the USS *Arizona* Preservation Project, which is a continuation of an interdisciplinary research program initiated in 1999. This project incorporates several disciplines, including corrosion control, water chemistry, structural

<sup>†</sup>Trade name.

obtained with a combination of three phases: aragonite ( $\text{CaCO}_3$ ), siderite ( $\text{FeCO}_3$ ), and magnetite ( $\text{Fe}_3\text{O}_4$ ). The results of numerous integrated intensity profiles across the concretion samples for the three minerals are shown in Figures 2 and 3. Siderite is dominant from shipside to near seaside, with aragonite becoming dominant at seaside. Magnetite was uniformly low from shipside but it increased near seaside. North's findings on iron-bearing concretions were consistent with these results.<sup>2</sup> In addition to the concretion, a thin layer of oxide-containing minerals exists between the concretion and the hull metal. This layer is normally 2 to 5 mm (0.08 to 0.20 in.) thick and is identified as a mixture of compounds, including chloride-containing akaganeite [ $\text{Fe}_8(\text{O},\text{OH})_{16}\text{Cl}_{1.3}$ ] and iron chloride hydrate ( $2\text{FeCl}_{3.7}\cdot\text{H}_2\text{O}$ ), as well as goethite [ $\text{FeO}(\text{OH})$ ], lepidocrocite [ $\text{FeO}(\text{OH})$ ], and magnetite  $\text{Fe}_3\text{O}_4$ .

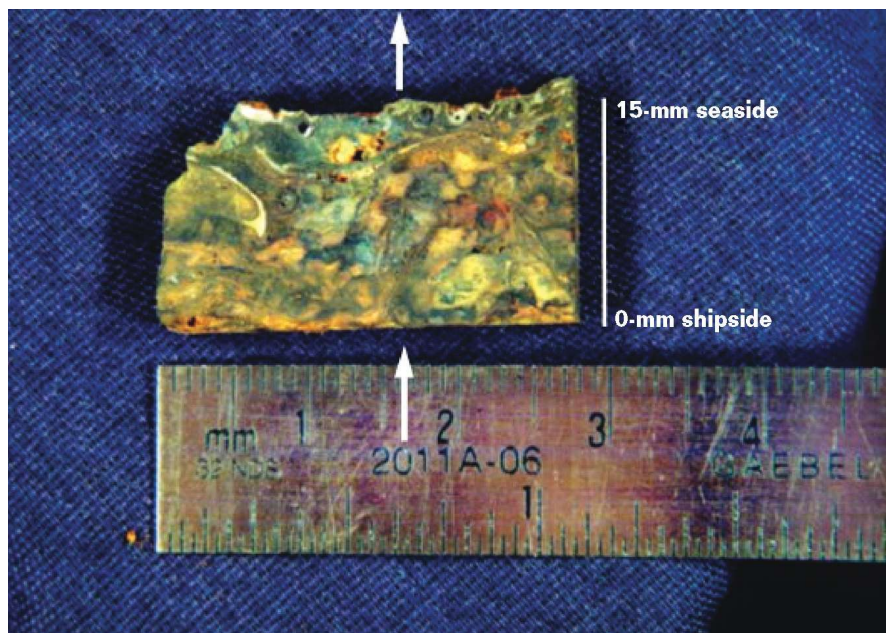
#### APPLICATION OF THE POURBAIX DIAGRAM

The iron/water/carbon dioxide ( $\text{CO}_2$ ) Pourbaix diagram (Figure 4) is useful as an aid to identifying corrosion products and reactions that occur from the metal surface into the concretion.<sup>6</sup> Typical  $E_{\text{corr}}$ /pH measurements taken from shipside to seaside,<sup>7</sup> superimposed on Figure 4, confirm the presence of  $\text{FeCO}_3$  and  $\text{Fe}_3\text{O}_4$ . Siderite appears at the lowest  $E_{\text{corr}}$ /pH values, followed by magnetite at slightly higher  $E_{\text{corr}}$ /pH values. Iron as  $\text{Fe}^{+2}$  appears at the lower left. These observations are consistent with Figure 2, indicating siderite from shipside into the concretion, and also with Figure 3, indicating magnetite near the seaside.

#### CONCRETION EQUIVALENT CORROSION RATE (CECR)

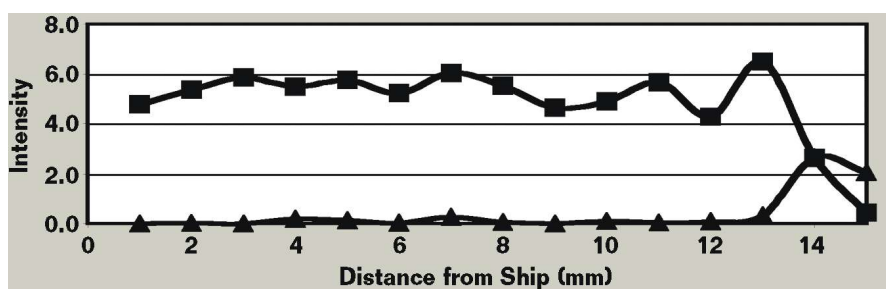
The identical slice used for XRD patterns was also used for an environmental scanning electron microscopy (ESEM) observation.<sup>5</sup> The data collected consisted of structural images from back-scattered electrons and chemical images of the same area collected from fluorescence radiation of the particular element. The major

FIGURE 1



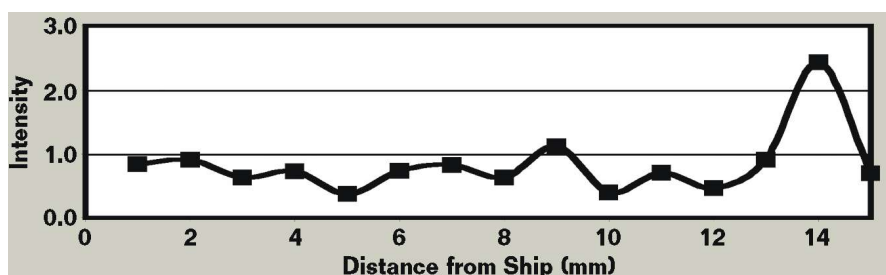
XRD measurements were made at 1-mm intervals along the cross section of the concretion sample to analyze the phases present in USS *Arizona* concretion.

FIGURE 2



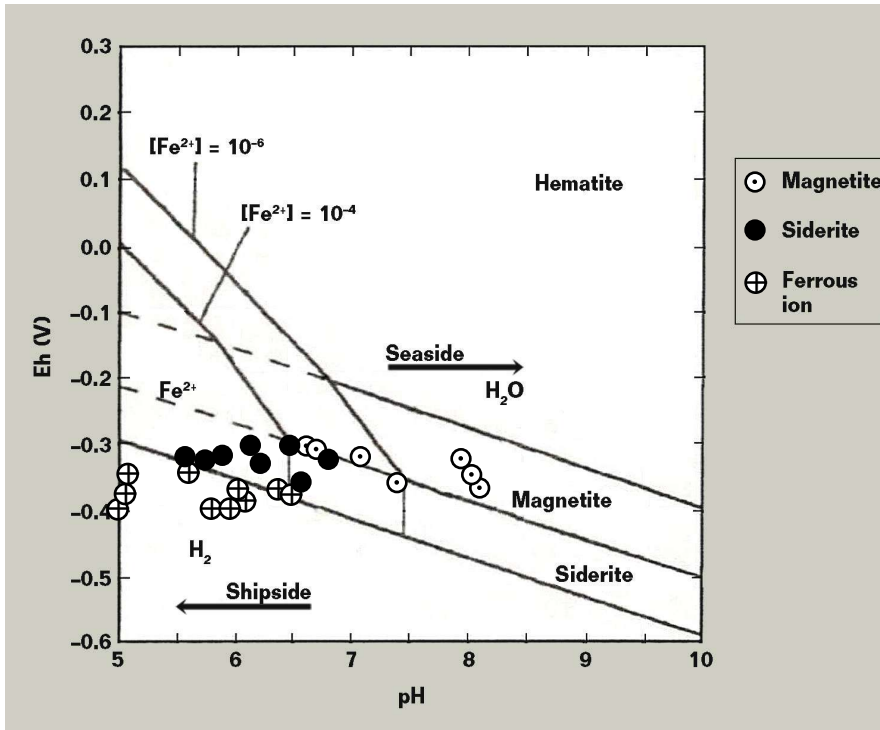
XRD intensity profiles for siderite (upper) and aragonite (lower) across USS *Arizona* concretion from shipside to seaside.

FIGURE 3



XRD intensity profiles for magnetite across USS *Arizona* concretion from shipside to seaside.

FIGURE 4



Potential-pH stability fields and superimposed potential and XRD scan data across USS Arizona concretion. Fe-H<sub>2</sub>O-CO<sub>2</sub> system at 25°C, 1 atm pressure.<sup>6</sup>

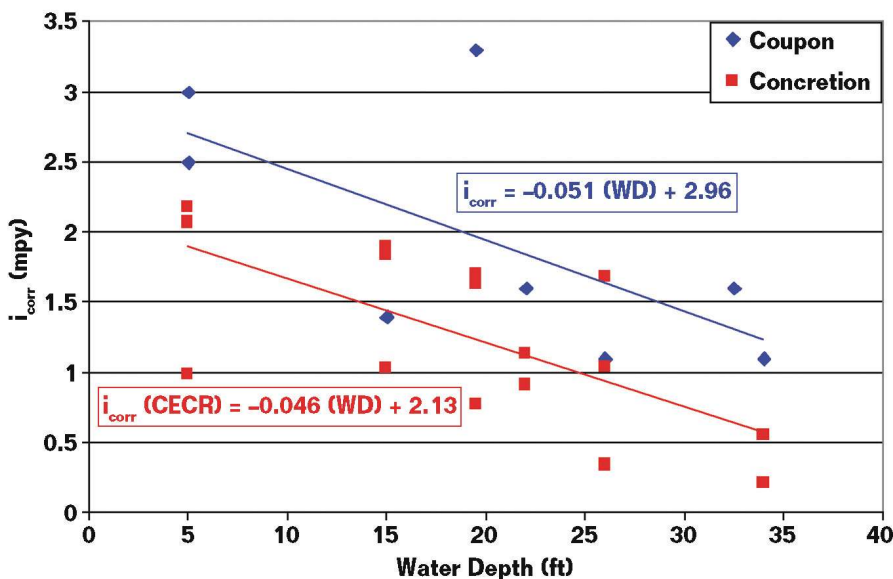
elements imaged were Fe, Ca, O, Cl, C, and S. Eleven positions were probed across the concretion from shipside to seaside and reported in wt% and atm%. A graphical integration of iron content at 11 positions across the concretion revealed a mean iron content of ~50 wt%, which is in good agreement with North.<sup>2</sup> These data confirm that finding the correlation between the direct corrosion rate and concretion iron content is a viable approach to estimating corrosion rate.<sup>1</sup> An expression of this correlation is given by:

$$i_{\text{corr}} = \frac{0.5 \times \rho \times \text{wt\% Fe} \times d}{t} \quad (1)$$

where  $i_{\text{corr}}$  is the concretion equivalent corrosion rate (CECR), mpy;  $\rho$  is the concretion density, gr/cm<sup>3</sup>; wt% Fe is the wt% iron in the concretion;  $d$  is the concretion thickness, cm; and  $t$  is time, years.

Concretion density according to ASTM D 792-00<sup>8</sup> was measured on samples taken from 17 exterior hull locations midships between Frames 70 and 90. Density and thickness for each sample were measured immediately after surfacing on site at USS Arizona Memorial and remeasured at the University of Nebraska-Lincoln (UNL) metallurgical engineering laboratories. Wet chemical analysis for total iron was conducted in the analytical chemistry laboratories at UNL. Using Equation (1), the complete data set for all 17 concretion samples was converted to CECR and was plotted as the lower (red) line in Figure 5. The direct corrosion rates measured from metal coupons, taken from Part 1 of this article and shown in blue, are a factor of ~1.6 higher than that predicted from Equation (1). The reasons for the difference are: 1) a high initial corrosion rate producing soluble iron lost to seawater prior to the accumulation of concretion, 2) the formation of an iron oxide/chloride layer not captured by the concretion sample, and 3) the possible loss of iron due to interior hull-side corrosion. Incorporating the correction factor of 1.6 into Equation (1), the following equation defines the CECR as it applies to USS Arizona data:

FIGURE 5



Comparison of the corrosion rate on USS Arizona compiled from both coupon data and concretion iron content measurements as a function of water depth.



$$i_{\text{corr}} = \frac{K \times \rho \times \text{wt}\% \text{ Fe} \times d}{t} \quad (2)$$

where,  $K = 0.5 \times 1.6 = 0.8$  for  $i_{\text{corr}}$  in mpy, and  $K = 20.32$  for  $i_{\text{corr}}$  in  $\mu\text{m}/\text{y}$ . The trend-line for Equation (2) closely tracks the blue line (coupon) in Figure 5.

## Conclusions

X-ray and electron diffraction data confirm the viability of the CECR to determine the corrosion rate. Calculated CECRs between Frames 70 and 90 are consistent with the coupon analysis at Frame 75. The CECR is based on analyzing concretion from USS *Arizona*. Further analysis is required at other sites to confirm the correction factor of 1.6 where variables such as temperature, flow velocity, organic activity, pH, salinity, and oxygen concentration may be different. A correction factor for other sites may be derivable from such measurements on site where testing is ongoing and further refinements may be necessary. At this stage of the research, however, concretion analysis appears to be a viable proxy for the direct sampling of hull metal to minimize impact on the ship's existing structure.

## Acknowledgments

The following organizations contributed funding to this research: Legacy Resources Management Fund, Department of Defense, Submerged Resources Center, National Park Service, USS *Arizona* Memorial and *Arizona* Memorial Museum Association, University of Nebraska Foundation, Emeriti Association, and the Department of Mechanical Engineering at UNL. Special thanks are extended to Robert DeAngelis, Air Force Research Laboratory, Eglin Air Force Base, for x-ray diffraction; Richard Schalek, Michigan State University for ESEM analysis; John Makinson, Rail Sciences; Titan Maritime Industries; Dania Florida; and U.S. Navy, Pearl Harbor, who are acknowledged for considerable contributions.

The following individuals are acknowledged for helpful advice and/or equip-

ment loan: Gary Matlock, GMC Electrical; Steve West, Thermo Electron; and Jon Johnson, FilmTec Corp. This article is dedicated to the memory of William N. Weins.

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